



Shielding ceria based catalysts from SO₂ poisoning in NH₃-SCR reaction: Modification effect of acid metal oxides

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ABSTRACT

Modifying CeO₂ with acid sites is a common strategy for designing efficient catalysts for the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR of NO_x). However, the effect of acid metal oxide modification on the SO₂ resistance of CeO₂ has not been well revealed. In this work, it was found that the SO₂ resistance of CeO₂ modified with several acid metal oxides (*i.e.*, MoO₃, WO₃ and Nb₂O₅), followed an order of Mo/CeO₂ ≥ W/CeO₂ > Nb/CeO₂. Further systematic characterizations revealed that Mo-OH and W-OH on CeO₂ as Brønsted acid sites could better inhibit the SO₂ adsorption and the sulfation of active sites than highly dispersed NbO_x mainly as Lewis acid sites because NH₄⁺ coordinated to Brønsted acid sites could help trap SO₂ to form ammonium sulfates rather than metal sulfates. The findings in this work provided important guidance for the design of efficient catalysts with superior SO₂ resistance performance.

1. Introduction

Nitrous oxides (NO_x) emitted by both mobile and stationary sources have been considered one of the most dangerous air pollutants, which could result in serious air pollution problems (*e.g.*, photochemical smog, haze and acid rain, *etc.*) [1,2]. Driven by the tightening policies and increasing environmental awareness, various techniques, such as selective non-catalytic reduction of NO_x (SNCR), urea or ammonia selective catalytic reduction of NO_x (urea-SCR or NH₃-SCR), *etc.*, have been developed to realize elimination of NO_x [3–5]. Among them, NH₃-SCR of NO_x was the most efficient one, and the efficient catalyst is the core of NH₃-SCR technique [6,7]. By far, the most popular commercial catalyst for NH₃-SCR is V₂O₅-WO₃(MoO₃)/TiO₂, which exhibited superior deNO_x efficiency as well as satisfactory resistance to SO₂ poisoning at 300–400 °C [8,9]. However, the relatively poor low-temperature

activity and the biological toxicity posed by vanadium have led researchers to seek an alternative catalyst with enhanced low-temperature activity and satisfactory environmental friendliness.

Recently, environmentally benign ceria (CeO₂) based catalytic materials with superior redox properties have caught the attention of researchers for their potential in NH₃-SCR of NO_x [10–14]. Since the NH₃-SCR reaction was composed of two half reactions, *i.e.*, redox cycle and acidity cycle, to enhance the NH₃-SCR performance of CeO₂ based materials, modifying CeO₂ with acid metal oxides as new acid sites for NH₃ adsorption/activation has been taken as the most effective strategy. For example, Peng *et al.* reported that CeO₂ doped with WO₃ exhibited superior NH₃-SCR activity because WO₃ species could act as acid sites to facilitate the adsorption and activation of NH₃ [15]. Similarly, CeZrO_x catalysts modified with Nb₂O₅ and MoO₃ were also found to exhibit enhanced NH₃-SCR activity due to the improved surface acidity

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[16–18]. Moreover, as reported by us previously, besides using as acid sites for NH_3 adsorption, CeO_2 based materials modified with different acid metal oxides (e.g., WO_3 , MoO_3 and Nb_2O_5 , etc.) showed different adsorption properties to reactant molecules, especially NO_x [19,20]. Specifically, highly dispersed WO_3 and MoO_3 could hinder the adsorption of NO_x on CeO_2 , while Nb_2O_5 deposited on CeO_2 showed much less inhibition effect on the NO_x adsorption. It was also found that CeO_2 modified with MoO_3 exhibited superior resistance to SO_2 adsorption, the first step in the SO_2 poisoning progress on NH_3 -SCR catalysts [21–23], thus helping alleviate SO_2 poisoning of CeO_2 . Inspired by this, it was proposed that the modification with different acid metal oxides could change the adsorption characteristics of SO_2 on CeO_2 to different degrees, then generate different SO_2 resistance performance. Since improving the SO_2 resistance of CeO_2 based catalysts has become one of

$$\text{N}_2 \text{ selectivity (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100\%$$

the hottest topics in the practical application of CeO_2 in low temperature NH_3 -SCR of NO_x and some other important reactions in the energy and environmental catalysis field, it is undoubtedly important to reveal the role of different metal oxides in shielding CeO_2 from SO_2 poisoning.

In this work, aimed at revealing the promotion effect of acid metal oxides modification on the NH_3 -SCR activity and SO_2 resistance ability of CeO_2 , and finding the most suitable acid metal oxide to achieve better SO_2 resistance, a series of CeO_2 catalysts modified with the optimal loadings of WO_3 , MoO_3 and Nb_2O_5 were selected as model catalysts, and systematic catalytic performance/ SO_2 resistance evaluation, various characterizations as well as mechanism study were conducted. It was deeply revealed that highly dispersed MoO_3 could better shield CeO_2 from SO_2 poisoning than highly dispersed WO_3 and Nb_2O_5 in NH_3 -SCR reaction, which provided important guidance for the design of efficient catalysts with superior SO_2 resistance performance.

2. Materials and experimental methods

2.1. Catalyst preparation

WO_3/CeO_2 , $\text{MoO}_3/\text{CeO}_2$ and $\text{Nb}_2\text{O}_5/\text{CeO}_2$ catalysts used in this work were prepared by wetness impregnation method. The CeO_2 support was prepared by thermal decomposition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in air at 550°C for 4 h, with a ramping rate of $2^\circ\text{C}\cdot\text{min}^{-1}$. To deposit WO_3 , MoO_3 and Nb_2O_5 onto CeO_2 , a certain amount of the precursors of WO_3 ($\text{H}_4\text{O}_4\text{N}_{10}\text{O}_{41}\text{W}_{12} \cdot n\text{H}_2\text{O}$), MoO_3 ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) or Nb_2O_5 ($\text{C}_4\text{H}_4\text{NNbO}_9 \cdot n\text{H}_2\text{O}$) and oxalic acid (molar ratio of metals in precursor to oxalic acid was 1:1.5) were first dissolved in deionized water under vigorous stirring, and then CeO_2 support was added to the solution. Afterwards, the mixture was evaporated at 110°C under vigorous stirring. The obtained solid was dried at 110°C for 12 h, followed by the calcination in air at 500°C for 4 h, with a ramping rate of $2^\circ\text{C}\cdot\text{min}^{-1}$. The prepared WO_3/CeO_2 , $\text{MoO}_3/\text{CeO}_2$ and $\text{Nb}_2\text{O}_5/\text{CeO}_2$ catalysts were denoted as $x\text{W}/\text{CeO}_2$, $y\text{Mo}/\text{CeO}_2$ and $z\text{Nb}/\text{CeO}_2$ (x , y or z mmol per $1000\text{ m}^2\text{ CeO}_2$ = The loading of WO_3 , MoO_3 or Nb_2O_5 on CeO_2). According to the results of further catalytic performance evaluation, WO_3/CeO_2 , $\text{MoO}_3/\text{CeO}_2$ and $\text{Nb}_2\text{O}_5/\text{CeO}_2$ catalysts with optimal loadings were denoted as W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 , respectively. For further catalytic performance evaluation, the catalysts were tableted and sieved into 40–60 mesh.

The catalysts after SO_2 resistance test were denoted as W/CeO_2 -used, Mo/CeO_2 -used and Nb/CeO_2 -used. The catalyst after regeneration was denoted as W/CeO_2 -R, Mo/CeO_2 -R and Nb/CeO_2 -R.

2.2. Catalytic performance evaluation

The NH_3 -SCR activity and N_2 selectivity on the prepared catalysts were evaluated on a fixed-bed quartz tube reactor. For each test, 200 mg catalyst was loaded into the middle of the quartz tube. The feeding gas consisted of 500 ppm NO , 500 ppm NH_3 , 5% O_2 and 100 ppm SO_2 (when used), using N_2 as balance. For all tests, the total flow rate was $200\text{ mL}\cdot\text{min}^{-1}$, giving a WHSV (weight hourly space velocity) of $60,000\text{ mL g}^{-1}\text{ h}^{-1}$. The effluent gas was continuously analyzed on an online Thermofisher iS10 FT-IR spectrometer equipped with a 2 m path-length gas cell (250 mL volume). The NO_x conversion and N_2 selectivity were determined according to the following equations:

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%$$

2.3. Catalyst characterization

The specific surface area of samples was measured by N_2 -physorption at 77 K on a Micromeritics ASAP-2020 analyzer via Brunauer-Emmet-Teller (BET) method. Before each test, the sample was degassed in vacuum at 300°C for 3 h.

X-ray powder diffraction (XRD) patterns were collected on a Philips X'pert Pro diffractometer (APL, Switzerland) using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). The X-ray tube was operated at 40 kV and 40 mA. The 2θ range was from 10 to 80° . The scan step was set as 0.02° . The scan speed was controlled at $10^\circ\cdot\text{min}^{-1}$.

Raman spectra were collected on a HORIBA (Japan) LabRAM Aramis Raman spectrometer equipped with an Ar^+ laser beam. The emission line was set at 532 nm, and the output power was 10 mW.

Thermogravimetry analysis-mass spectrum (TG-MS) analysis and differential thermal analysis (DTA) were conducted on Netzsch thermoanalyzer STA 449 C instrument. In each test, samples were heated from room temperature to 950°C with a ramping rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in N_2 flow ($60\text{ mL}\cdot\text{min}^{-1}$). The tail gas was analyzed by an online mass spectrometer.

H_2 -temperature-programmed reduction (H_2 -TPR) experiments were performed on a quartz U-tube reactor connected to an online thermal conductivity detector (TCD). In each test, ca. 10 mg samples were loaded into the U-tube. 7% H_2/Ar ($10\text{ mL}\cdot\text{min}^{-1}$) was used as reducing reagent. Prior to the reduction process, the sample was pretreated by N_2 flow ($10\text{ mL}\cdot\text{min}^{-1}$) at 200°C for 1 h, and then cooled to room temperature. The reduction process was measured from room temperature to 950°C , with a ramping rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. H_2O in the tail gas was removed by a cold trap before being passed into the TCD.

X-ray photoelectron spectroscopy (XPS) experiments were performed on a PHI 5000 Versa Probe system. Monochromatic $\text{Al K}\alpha$ ($h\nu = 1486.6\text{ eV}$) was used as the radiation of the instrument, and the acceleration power was 15 kW. The binding energies of all elements were calibrated with C 1 s at 284.6 eV.

NH_3 -temperature-programmed desorption (NH_3 -TPD) experiments were conducted on a fixed-bed quartz tube reactor connected with an online Thermofisher iS10 FT-IR spectrometer equipped with a 2 m path-length gas cell (250 mL volume). In each test, ca. 100 mg catalyst was loaded into the quartz tube, followed by pretreatment in Ar flow ($100\text{ mL}\cdot\text{min}^{-1}$) at 300°C for 30 min. Then the catalyst was saturated with NH_3 at room temperature. Afterwards, Ar flow ($100\text{ mL}\cdot\text{min}^{-1}$)

was switched on to remove the weakly adsorbed NH_3 . Finally, the catalyst was heated linearly from room temperature to 600 °C in Ar flow ($100 \text{ mL} \cdot \text{min}^{-1}$) with a ramping rate of $5^\circ \text{C} \cdot \text{min}^{-1}$.

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) experiments were carried out on a Nicolet Nexus 5700 FTIR spectrometer equipped with an MCT detector. In each test, ca. 50 mg catalyst was loaded into the DRIFTS cell, pressed and mounted. Then the catalyst was pretreated with N_2 flow at 450 °C for 1 h. The background spectra of samples at different temperatures were collected during the cooling process and automatically subtracted from the sample spectra. The feeding gas ($50 \text{ mL} \cdot \text{min}^{-1}$) consisted of 3000 ppm NH_3 (when used), 3000 ppm NO (when used), 5 vol% O_2 (when used) and 100 ppm SO_2 (when used), using N_2 as balance. The spectra were collected from 650 to 4000 cm^{-1} , with a spectral resolution of 4 cm^{-1} for 32 scans. The spectra were presented in the form of Kubelka-Munk.

3. Results And Discussion

3.1. Activity and SO_2 resistance of catalysts

The NH_3 -SCR activity on $x\text{W}/\text{CeO}_2$, $y\text{Mo}/\text{CeO}_2$ and $z\text{Nb}/\text{CeO}_2$ was first tested and illustrated in Fig. S1. After the modification with WO_3 , MoO_3 and Nb_2O_5 , the NH_3 -SCR activity on CeO_2 was significantly enhanced, which should be mainly resulted from the improvement of surface acidity [24–26]. $x\text{W}/\text{CeO}_2$, $y\text{Mo}/\text{CeO}_2$ and $z\text{Nb}/\text{CeO}_2$ also showed much higher N_2 selectivity than CeO_2 (Fig. S2). The optimal loadings of metal oxides for $x\text{W}/\text{CeO}_2$, $y\text{Mo}/\text{CeO}_2$ and $z\text{Nb}/\text{CeO}_2$ to achieve the best NH_3 -SCR activity were 10, 14 and 18 mmol per 1000 m^2 CeO_2 , respectively (Fig. 1a). CeO_2 catalysts modified with

optimal loadings of WO_3 , MoO_3 and Nb_2O_5 in the following sections were denoted as W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 for convenience.

Although a variety of CeO_2 based catalysts have been reported to exhibit superior NH_3 -SCR activity even at low temperature ($150\text{--}200^\circ \text{C}$), the severe SO_2 poisoning effect made them far away from the practical application, especially in the low temperature range. Herein, to investigate the SO_2 resistance ability of W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 at low temperatures, NH_3 -SCR activity on them was evaluated at 175°C in the presence of 100 ppm SO_2 . As shown in Fig. 1b, once SO_2 was introduced to the samples at 175°C , the NO_x conversions on W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 all declined accordingly, which might be related to the poisoning of active sites by SO_2 or the coverage of catalyst surface by ammonium sulfates, such as NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ [27,28]. However, it is interesting that CeO_2 modified with different acid metal oxides showed different deactivation trends. To better evaluate the rate of deactivation resulted from SO_2 poisoning, the NO_x conversion as a function of time was normalized based on the initial NO_x conversion on fresh samples (Fig. 1c). It was found that the de NO_x efficiency of Nb/CeO_2 decreased by 80% in 8 h, much worse than that of W/CeO_2 (55%) and Mo/CeO_2 (55%), indicating that WO_3 - CeO_2 and MoO_3 - CeO_2 paired sites could better survive than Nb_2O_5 - CeO_2 paired sites in the presence of SO_2 . The reasons for the slight increase in the NO conversion on CeO_2 at the beginning of adding SO_2 should be related to the deposition of sulfate species, which could act as Brønsted acid sites for the adsorption and activation of NH_3 [29].

Considering that the affinity of catalysts surface for SO_2 as well as the SO_2 adsorption amount could determine the SO_2 resistance performance of NH_3 -SCR catalysts [21–23], $\text{SO}_2 + \text{O}_2$ penetration experiments were conducted, and the results were demonstrated in Fig. 1d. It was observed

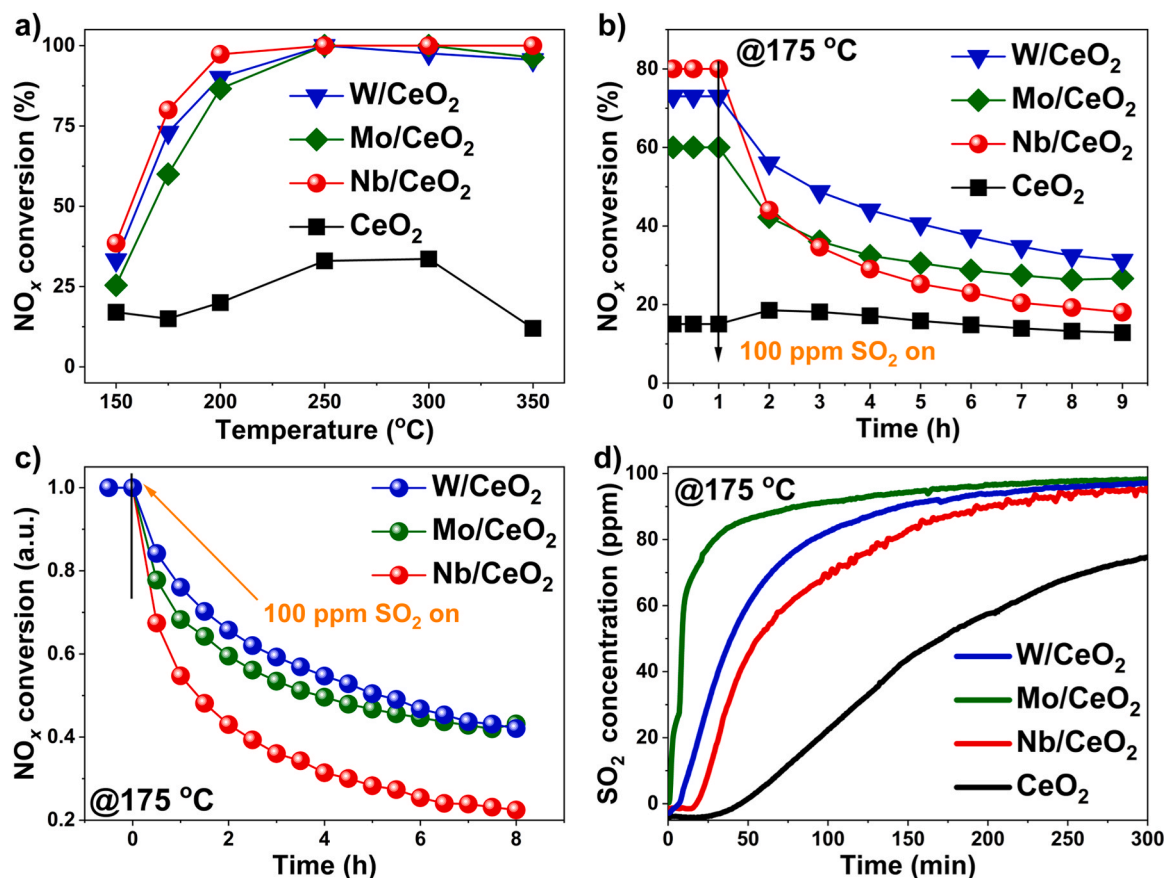


Fig. 1. a) NO_x conversions on CeO_2 , W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts in NH_3 -SCR reaction; b) NO_x conversions on CeO_2 , W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts in the presence of 100 ppm SO_2 at 175°C ; c) Normalized NO_x conversions on W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts; d) SO_2 concentration in the outlet gas during the 100 ppm $\text{SO}_2 + 5\%$ O_2 penetration experiments at 175°C . Reaction condition: 500 ppm NH_3 , 500 ppm NO , 5% O_2 , 100 ppm SO_2 (when used), Ar as balance.

that acid metal oxides loaded on CeO_2 could alleviate the adsorption of SO_2 . Furthermore, Mo/CeO_2 and W/CeO_2 could be saturated with SO_2 much faster than Nb/CeO_2 , indicating that MoO_3 or WO_3 could better inhibit the adsorption of SO_2 on CeO_2 than Nb_2O_5 , which provided meaningful guidance for developing efficient CeO_2 based catalysts with better SO_2 resistance.

3.2. Structure of the catalysts

To better reveal the reasons for different SO_2 resistance performance of W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 , systematic characterizations were conducted to investigate their structures. XRD patterns for CeO_2 , xW/CeO_2 , yMo/CeO_2 and zNb/CeO_2 were first collected (Fig. S3). For all CeO_2 catalysts modified with optimal loadings of acid metal oxides, all diffraction peaks were assigned to cubic fluorite CeO_2 (JCPDS 34-0394), and no additional peak assigned to crystalline acid metal oxides was observed, indicating that W, Mo and Nb species were highly dispersed on CeO_2 .

According to the results of N_2 -physisorption experiments, W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 showed comparable specific surface area (SSA) and pore volume (Table S1), suggesting that SSA and pore volume would not contribute to the difference in their SO_2 resistance performance. The slight decrease ($< 10 \text{ m}^2 \cdot \text{g}^{-1}$) in the SSA of CeO_2 after the deposition of acid metal oxides should be mainly due to the further calcination at 500°C for 4 h and slight pore blocking. Moreover, after the SO_2 resistance test, almost no change was observed in the SSA of W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 , indicating good structure stability in the presence of SO_2 .

To further study the surface structure of the prepared catalysts, Raman spectra of xW/CeO_2 , yMo/CeO_2 and zNb/CeO_2 were collected. For all samples, an intensive band at ca. 465 cm^{-1} and a broad band at ca. 600 cm^{-1} were observed (Fig. 2a and Fig. S4), which were related to the F_{2g} vibration mode of CeO_2 and oxygen defects (D band), respectively [30,31]. After the deposition of WO_3 onto CeO_2 , two bands at 808 and 975 cm^{-1} emerged as the loadings increased, which could be assigned to W-O-Ce stretching vibrations and surface dispersed WO_3 species (Fig. S4a) [32–34]. When the WO_3 loadings further increase to $12 \text{ mmol per } 1000 \text{ m}^2 \text{ CeO}_2$, several bands assigned to crystalline WO_3 ($274, 330, 718 \text{ cm}^{-1}$) were observed, matching well with the results of

XRD (Fig. S3b). For yMo/CeO_2 catalysts (Fig. S4c), several bands at $700\text{--}1000 \text{ cm}^{-1}$ could be clearly observed, which were attributed to the stretching vibration of Mo-O-X (X = Mo or Ce) and the surface molybdena species, according to the previous report [20,24,35]. With the increase of MoO_3 loading amount, a new band at 959 cm^{-1} emerged gradually and the band at 922 cm^{-1} disappeared, which was related to the formation of surface polymeric molybdena species [36]. Bands assigned to bulk MoO_3 were not observed on all yMo/CeO_2 catalysts, which was consistent with the result of XRD. In Fig. S4e, a broad band ranging from 750 to 950 cm^{-1} was observed on zNb/CeO_2 , which was mainly related to polymeric niobium oxides species composed of moderately distorted octahedral $[\text{NbO}_6]$ structures with terminal Nb=O bonds (864 cm^{-1}) [25,37,38]. In short summary, for WO_3/CeO_2 , $\text{MoO}_3/\text{CeO}_2$ and $\text{Nb}_2\text{O}_5/\text{CeO}_2$ catalysts with optimal loadings, the acid metal oxides on CeO_2 were mainly in the form of highly dispersed polymeric metal oxides. Based on the results of Raman spectra (Fig. 2a) and previous reports [15,39,40], the configurations WO_3 , MoO_3 and Nb_2O_5 species on W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 were proposed and demonstrated in Fig. 2b.

Moreover, the strong interaction between these highly dispersed acidic metal oxides and CeO_2 support might also contribute to the formation of more surface oxygen vacancies, which was further supported by the calculated relative concentration of oxygen vacancies on CeO_2 , W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts according to their Raman spectra (Table S1, Relative concentration of oxygen defects = $I_D/I_{F_{2g}}$, I_D and $I_{F_{2g}}$ represented the peak area of D bands and CeO_2 F_{2g} bands, respectively). The formation of more surface oxygen vacancies could better facilitate the activation of reactants, which could also account for the significantly improved catalytic performance of CeO_2 after the modification with acid metal oxides.

3.3. Sulfate species formed on CeO_2 , W/CeO_2 , Mo/CeO_2 and Nb/CeO_2

It has been reported that H_2 -TPR technique could be used not only to explore the reducibility of the catalysts but also to investigate the sulfate species formed on catalysts after SO_2 resistance test. As shown in Fig. 3a, three H_2 -consumption peaks were observed on the H_2 -TPR profiles for CeO_2 . Peak α (ca. 420°C), peak β (ca. 540°C) and peak γ (ca. 770°C) could be attributed to the reduction of surface chemisorbed oxygen

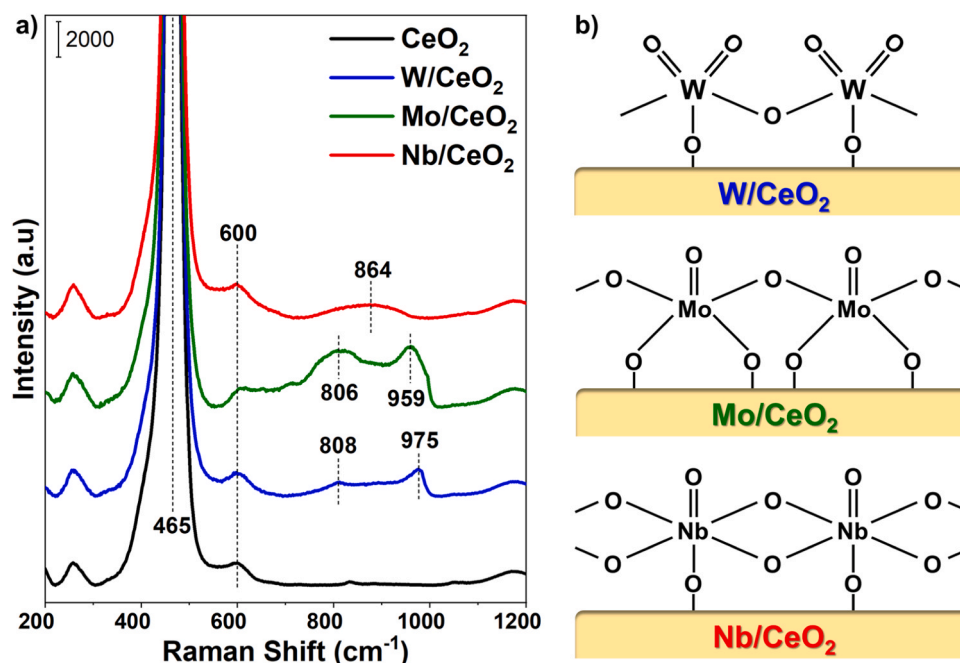


Fig. 2. a) Raman spectra for CeO_2 , W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts. b) Proposed configurations of WO_3 , MoO_3 and Nb_2O_5 species on CeO_2 .

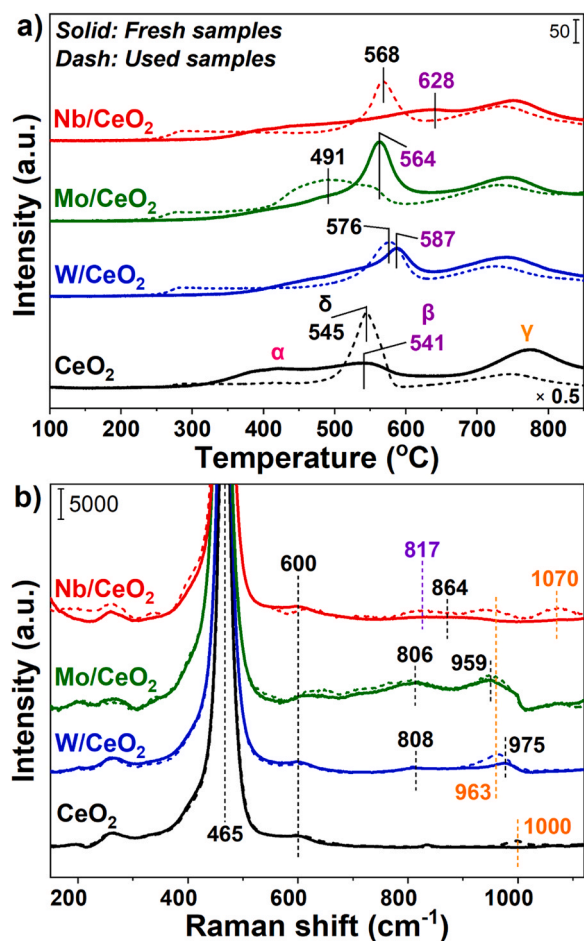


Fig. 3. a) H₂-TPR profiles and b) Raman spectra for fresh and used CeO₂, W/CeO₂, Mo/CeO₂ and Nb/CeO₂ (Solid line: fresh samples, dash line: used samples).

species, surface Ce⁴⁺ and bulk CeO₂, respectively [41]. After the deposition of WO₃, MoO₃ and Nb₂O₅, peak β on W/CeO₂, Mo/CeO₂ and Nb/CeO₂ were all found to shift to higher temperatures, hinting at the formation of stronger interaction between highly dispersed acid metal oxides and CeO₂ [19,42]. As discussed above, highly dispersed acid metal oxides on CeO₂ all helped generate superior NH₃-SCR activity, however, W/CeO₂, Mo/CeO₂ and Nb/CeO₂ exhibited different SO₂ resistance performance due to their different adsorption properties for SO₂. Different from the H₂-TPR profiles for fresh samples, a new H₂-consumption peak at 490–580 °C (peak δ) was observed on the H₂-TPR profiles for all used samples, which could be assigned to the reduction of the deposited sulfate species. More interestingly, the reduction of sulfate species on Mo/CeO₂ occurred at much lower temperatures than those on CeO₂-used, W/CeO₂-used and Nb/CeO₂-used, indicating that highly dispersed MoO₃ species strongly interacting with CeO₂ support could better weaken the interaction between sulfate species (SO₄²⁻) and CeO₂ and inhibit the deep sulfation to form bulk sulfate species, thus significantly reducing the adsorption of SO₂ during the SO₂ resistance test [43,44].

To further investigate the impact of sulfate species on the states of dispersed acid metal oxides on W/CeO₂, Mo/CeO₂ and Nb/CeO₂, Raman spectra for those used catalysts were also collected (Fig. 3b). For CeO₂-used, a distinct peak at ca. 1000 cm⁻¹ assigned to surface sulfate species was observed. Similarly, for W/CeO₂, Mo/CeO₂ and Nb/CeO₂, the emerged band at ca. 963 and 1070 cm⁻¹ could also be attributed to the formation of sulfate species [45,46]. The almost negligible intensity of this band on Mo/CeO₂ further supported the viewpoint that much less

sulfate species were formed on Mo/CeO₂ comparing to W/CeO₂ and Nb/CeO₂. Moreover, a new band at ca. 817 cm⁻¹ related to the Nb-O symmetric modes of the NbO₄ tetrahedral structure was observed on Nb/CeO₂-used, suggesting that SO₂ could also react with octahedral [NbO₆] structure with terminal Nb=O bonds (864 cm⁻¹) to form NbO₄ tetrahedral structure. [47,48] The evolution of the surface structure of Nb/CeO₂ when exposed to SO₂-containing reaction flow could be one of the main reasons for its relatively poorer SO₂ resistance. As reported previously [19,49], Nb₂O₅ showed relatively better redox performance than MoO₃ and WO₃, well explaining that SO₂ could better react with Nb species on Nb/CeO₂ at a low temperature of 175 °C.

Based on the concentration of SO₂ in the outlet gas of SO₂ + O₂ adsorption experiment (Fig. 1d), it was proposed that the SO₂ adsorption capacity followed an order of Mo/CeO₂ < W/CeO₂ < Nb/CeO₂ < CeO₂. To further determine the amount of the sulfate species deposited on the catalysts after the SO₂ resistance test (Fig. 3a), TG-MS experiments were conducted. As shown in Fig. 4a-d, for all used catalysts, three weight loss steps were observed. According to previous reports, those three weight loss steps from low temperature to high temperature should be related to the desorption of adsorbed H₂O/NH₃, the decomposition of ammonium bisulfate (ABS, 2NH₄HSO₄ → 2NH₃ + 2H₂O + 2SO₂ + O₂) and the decomposition of Ce(SO₄)₂ or Ce₂(SO₄)₃ (Ce(SO₄)₂ → CeO₂ + 2SO₂ + O₂, Ce₂(SO₄)₃ → 2CeO₂ + 3SO₂ + O₂), respectively [46,50,51]. Interestingly, although the second step (300–550 °C) could be assigned to the decomposition of ABS, almost no SO₂ was detected in this range, which could be due to the re-adsorption of SO₂ by CeO₂ to generate extra sulfated CeO₂ species [29]. Based on this understanding, the weight loss during the third step could be used to compare the amount of sulfate species on the used catalysts.

As marked in Fig. 4, sulfate species on Mo/CeO₂-used (0.72%) were much less than those on W/CeO₂-used (1.27%) and Nb/CeO₂-used (1.50%), matching well with the expectation. The much more sulfate species on CeO₂-used (2.56%) further confirmed that highly dispersed acid metal oxides could efficiently shield CeO₂ from SO₂ poisoning, and highly dispersed MoO₃ species performed the best. Moreover, the amount of ABS formed on Mo/CeO₂ (0.50%) was higher than that on W/CeO₂-used (0.40%) and Nb/CeO₂-used (0.26%), suggesting that the total amount of sulfate species deposited on Mo/CeO₂-used is not only minimal, but also more in the form of ABS. Furthermore, it was observed that the SO₂-desorption peak on used Mo/CeO₂ was located at lower temperatures (714 °C) comparing to that on used W/CeO₂ (755 °C) and used Nb/CeO₂ (746 °C), suggesting that sulfated CeO₂ on used Mo/CeO₂ would decompose at lower temperature. Considering that the decomposition temperature (> 600 °C) of sulfated CeO₂ on all catalysts was much higher than the operation temperature of NH₃-SCR catalysts (< 500 °C), the lower desorption temperature of SO₂ on the used catalysts could not contribute to the better SO₂ resistance of Mo/CeO₂. However, the lower desorption temperature of SO₂ on Mo/CeO₂ suggested that Mo coordinated to Ce could weaken the interaction between CeO₂ and SO₂, thus inhibiting the adsorption of SO₂ on Ce sites. That is, the deep sulfation of metal sites (mainly Ce sites) on Mo/CeO₂ could be effectively retarded due to the easier reaction between NH₃ species adsorbed on Mo (Mo-O-NH₄) and SO₂ to generate ABS and inhibitory effect of Mo on the interaction between CeO₂ and SO₂.

ATR-FTIR experiments were performed to further determine the states of sulfate species on used catalysts. As shown in Fig. 5a, several bands assigned to various sulfate species were observed at 1626, 1165, 1127, 1108, 1055, 985, 952 and 894 cm⁻¹ were related to surface sulfate species and the bands at 1211 and 985 cm⁻¹ could be further assigned to the bulk sulfate species. The relatively lower intensity of these bands assigned to bulk sulfate species on Mo/CeO₂-used confirmed that Mo modification could better shield CeO₂ from deep sulfation. The bands at 952 and 894 cm⁻¹ not observed on CeO₂ could be related to SO₄²⁻ species adjacent to W, Mo or Nb sites. The intensive band at ca. 1429 cm⁻¹ could be attributed to NH₄⁺ in ABS, well supporting the viewpoint that abundant ABS was deposited on the catalysts in SO₂

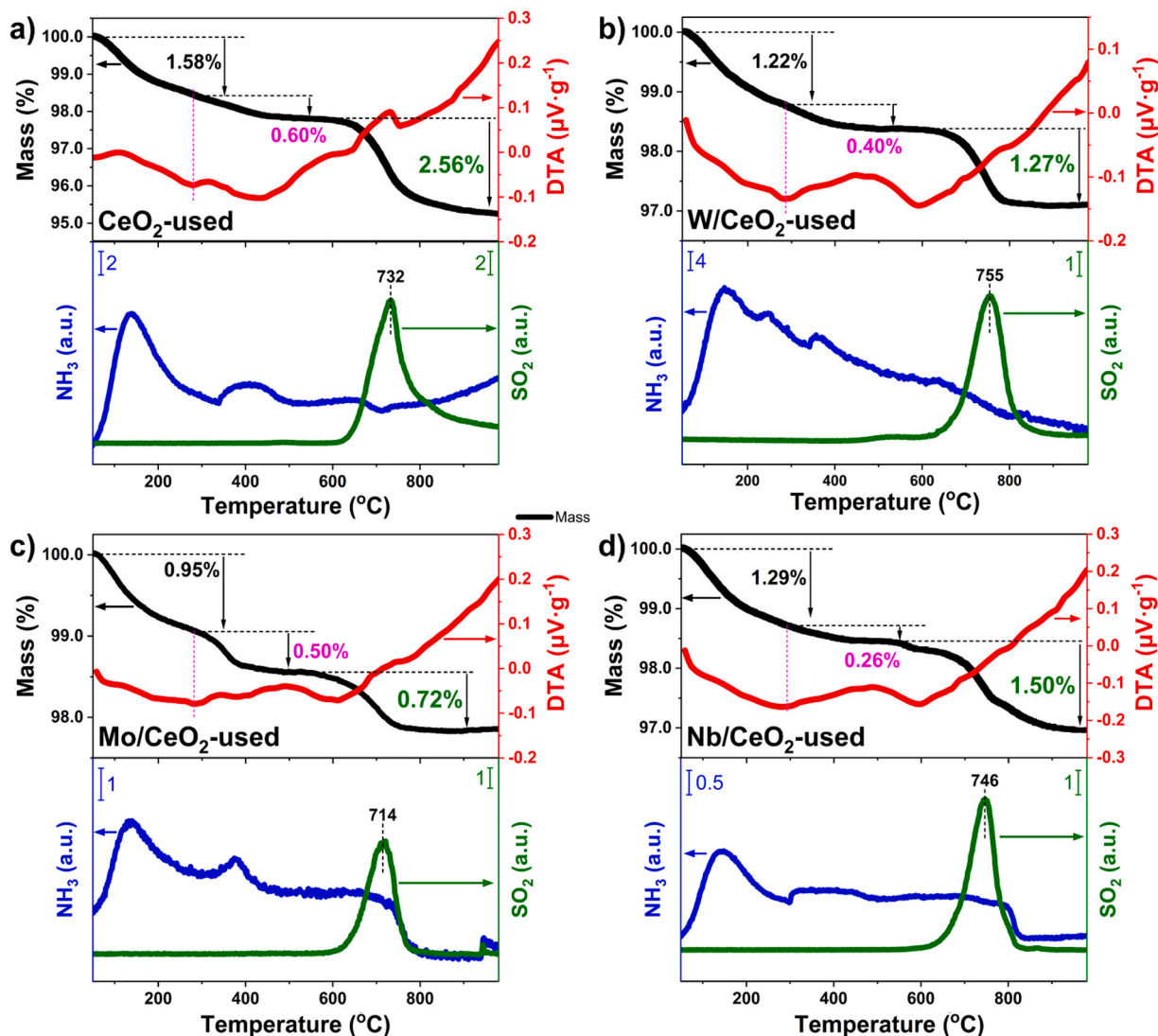


Fig. 4. TG-MS and DTA plots for a) CeO_2 -used, b) W/CeO_2 -used, c) Mo/CeO_2 -used and d) Nb/CeO_2 -used catalysts.

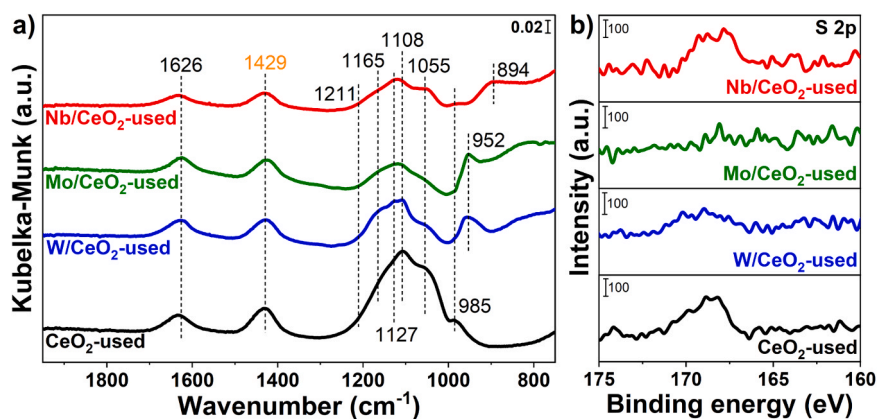


Fig. 5. a) ATR-FTIR spectra and b) S 2p XPS for used catalysts.

resistance test.

XPS experiments were conducted to further investigate the surface states as well as the amount of sulfur species on the used catalysts. As shown in Fig. 5b, the intensity of S 2p XPS followed an order of $\text{CeO}_2 > \text{Nb/CeO}_2 > \text{W/CeO}_2 > \text{Mo/CeO}_2$, in good consistency with the results

of TG-MS that the least number of sulfate species were deposited on Mo/CeO_2 in the SO_2 resistance test. The relative concentration of S element on different catalysts was also calculated and listed in Table 1. XPS for W 4f, Mo 3d and Nb 3d of fresh and used catalysts were also collected. As shown in Fig. S5a, the two peaks at ca. 37.3 eV (W 4f_{5/2}) and ca. 35.2 eV

Table 1
Surface element concentration and Chemical states determined by XPS.

Samples	Surface atomic concentration (%)				Ce ³⁺ /Total Ce (%)	O _a /Total O (%)
	W/Mo/Nb	Ce	O	S		
CeO ₂	-	22.2	77.8	-	16.0	36.6
W/CeO ₂	4.5	19.3	75.2	-	17.6	26.9
Mo/CeO ₂	6.5	16.6	76.9	-	16.3	24.4
Nb/CeO ₂	7.9	13.8	78.3	-	16.4	37.6
CeO ₂ -used	-	22.2	73.6	4.2	19.4	51.7
W/CeO ₂ -used	4.9	18.8	73.8	2.5	21.8	31.4
Mo/CeO ₂ -used	5.6	16.3	77.1	1.0	18.1	25.6
Nb/CeO ₂ -used	8.9	16.2	71.4	3.5	18.9	47.4

(W 4f_{7/2}) on W/CeO₂ could be assigned to the W⁶⁺ species. Similarly, the peaks observed on Mo 3d XPS for Mo/CeO₂ and Nb 3d XPS for Nb/CeO₂ could be assigned to Mo⁶⁺ and Nb⁵⁺ species, respectively [19,20]. After being used in the SO₂ resistance test, no significant change was observed on those peaks for W/CeO₂, Mo/CeO₂ and Nb/CeO₂, indicating that SO₂ and the deposited sulfate species had limited impact on the states of W, Mo or Nb species. Moreover, the surface concentration of W, Mo and Nb species showed no significant change after the SO₂ resistance (Table 1), indicating that the dispersion of these species didn't change significantly.

Ce 3d XPS for fresh and used catalysts were also collected and further analyzed to investigate the chemical states of Ce species (Fig. S6). After the modification with WO₃, MoO₃ and Nb₂O₅, the concentration of surface Ce³⁺ on CeO₂ increased slightly, which should be due to the strong interaction between W/Mo/Nb and CeO₂ and the resulting distortion of the CeO₂ surface lattice. The formation of more Ce³⁺ on modified CeO₂ also matched well with the results of Raman spectra that more surface oxygen vacancies were formed on CeO₂ after the modification with acid metal oxides, since the formation of Ce³⁺ was always accompanied by the generation of oxygen vacancies [52]. It was also found that more Ce³⁺ species were formed on all used catalysts comparing to fresh catalysts (Fig. S7a and Table 1). As reported previously, the generation of more Ce³⁺ species in SO₂-containing atmosphere was related to the reaction between SO₂ and CeO₂ (2CeO₂ + 3SO₂ + O₂ → Ce₂(SO₄)₃) [53].

O 1s XPS for fresh and used catalysts were shown in Fig. S8. Peak O_a (ca. 531.8 eV) and peak O_b (ca. 529.6 eV) could be attributed to the surface oxygen species and lattice oxygen species, respectively [54]. As listed in Table 1, more surface oxygen species were formed on used catalysts, which should be related to the sulfated species (ABS and sulfated CeO₂). Moreover, as demonstrated by Fig. S7b, the increase in the concentration of surface oxygen species on Mo/CeO₂ (from 24.4% to 25.6%) after the SO₂ resistance test was much lower than that on CeO₂ (from 36.6% to 51.7%), W/CeO₂ (from 26.9% to 31.4%) and Nb/CeO₂ (from 37.6% to 47.4%), also confirming the formation of less sulfate species on Mo/CeO₂.

3.4. Relationship between surface acidity and deposited metal oxides/sulfate species

Considering that the surface acidity of catalysts played an important role in NH₃-SCR reaction, NH₃-TPD experiments were conducted on fresh and used catalysts (Fig. 6a and b). For fresh CeO₂, two NH₃-desorption peaks were observed, which were marked in red (ca. 160 °C, peak α) and blue (ca. 242 °C, peak β). Peak α and peak β could be assigned to the desorption of NH₃ bound to acid sites with weak and medium strength, respectively [44,55]. After being modified with W, Mo or Nb, an additional intensive NH₃-desorption peak marked in green

was observed at higher temperatures (ca. 300 °C, peak γ), which should be related to the highly dispersed WO₃, MoO₃ and Nb₂O₅ species serving as Brønsted acid sites or Lewis acid sites with strong strength. The improvement of surface acidity could be one of the main reasons for the enhanced NH₃-SCR activity on CeO₂ modified with WO₃, MoO₃ and Nb₂O₅.

After the SO₂ resistance test, the total amount of desorbed NH₃ on used catalysts was much higher than that on fresh catalysts. As reported previously, the increase in the total amount of acid sites on sulfated catalysts could be due to the deposition of abundant sulfate species, which could act as Brønsted acid sites [56]. For used CeO₂, the presence of peak γ well supported the viewpoint that sulfated species deposited on CeO₂ could significantly enhance the surface acid species. However, NH₃ species (mainly in the form of NH₄⁺) linked to sulfate species showed poor activity at low temperatures (≤ 175 °C). In addition, the increase in the amount of acid sites on different catalysts followed an order of CeO₂ (113 μmol·g⁻¹) > Nb/CeO₂ (83 μmol·g⁻¹) > W/CeO₂ (71 μmol·g⁻¹) > Mo/CeO₂ (43 μmol·g⁻¹), which was also highly correlated to the amount of sulfate species deposited on these catalysts.

To further determine the type of acid sites on fresh and used catalysts, *in situ* DRIFTS of NH₃ adsorption experiments were conducted (Fig. 6c-j). Generally speaking, the peaks at 1100–1250 cm⁻¹ and 1580–1600 cm⁻¹ were mainly related to the NH₃ coordinated to Lewis acid sites (NH₃-L), while the peak at 1400–1500 cm⁻¹ and 1650–1800 cm⁻¹ could be attributed to NH₄⁺ species linked to Brønsted acid sites (NH₃-B). Other distinct bands should be ascribed to various nitrate species (Nit) generated by the oxidation of NH₃ species. For fresh CeO₂, NH₃ species were mainly adsorbed on Lewis acid sites, and NH₃-L species desorbed vigorously at low temperatures (< 200 °C), matching well with the results of NH₃-TPD (Fig. 6a). After the SO₂ resistance test, IR bands assigned to NH₃-L species were not observed at low temperatures, which should be related to the sulfation of surface CeO₂. The more intensive bands at ca. 1430 and 1680 cm⁻¹ observed on CeO₂-used should be related to NH₃ species adsorbed on sulfated CeO₂ (Brønsted acid sites). A new band at ca. 1300 cm⁻¹ assigned to NH₃ coordinated to Lewis acid sites was observed when the temperature increased to 200 °C or higher, due to the migration of NH₃ species from Brønsted acid sites to Lewis acid sites [57,58]. Different from what was observed on CeO₂, for fresh W/CeO₂ and Mo/CeO₂ catalysts, much more Brønsted acid sites were formed, and relatively weaker NH₃-L bands were observed on both W/CeO₂ and Mo/CeO₂ catalysts, suggesting that highly dispersed WO₃ and MoO₃ species on CeO₂ would mainly act as Brønsted acid sites. More interestingly, although intensive NH₃-B bands still could be observed on W/CeO₂-used and Mo/CeO₂-used, the intensity of NH₃-L bands on used catalysts was much weaker than that on fresh catalysts (Fig. 6e-h), which could be resulted from the sulfation of Lewis acid sites. Intensive NH₃-L and NH₃-B bands could be observed on fresh Nb/CeO₂ catalyst, which meant that highly dispersed NbO_x sites on CeO₂ could serve as both Lewis acid sites and Brønsted acid sites showing higher acid strength than those on bare CeO₂ (Fig. 6i). After the SO₂ resistance test, more Brønsted acid sites were formed on Nb/CeO₂ and the intensity of NH₃-L bands showed a sharp decrease simultaneously (Fig. 6j), indicating that both Nb and Ce sites were sulfated or covered by ammonium sulfates. In short summary, W/Mo/Nb modification could greatly enhance the surface acidity of CeO₂ from the aspect of amount and strength. After exposure to the SO₂-containing reaction stream, the surface sulfation of the catalysts would lead to an increase in Brønsted acid sites and a significant loss of Lewis acid sites.

According to the results of Raman spectra, TG-MS, ATR-FTIR, XPS and (*in situ*) NH₃-TPD experiments, the surface states of the used catalysts could be proposed. As shown in Fig. 7a, after the SO₂ resistance test, abundant surface sulfate species (ceric sulfates and ammonium sulfate species) were formed. After being modified with acid metal oxides, the amount of sulfate species deposited on CeO₂ decreased to different degrees, due to their shielding effect. For W/CeO₂ and Mo/CeO₂ catalysts (Fig. 7b and c), surface Brønsted acid sites (W-OH or Mo-

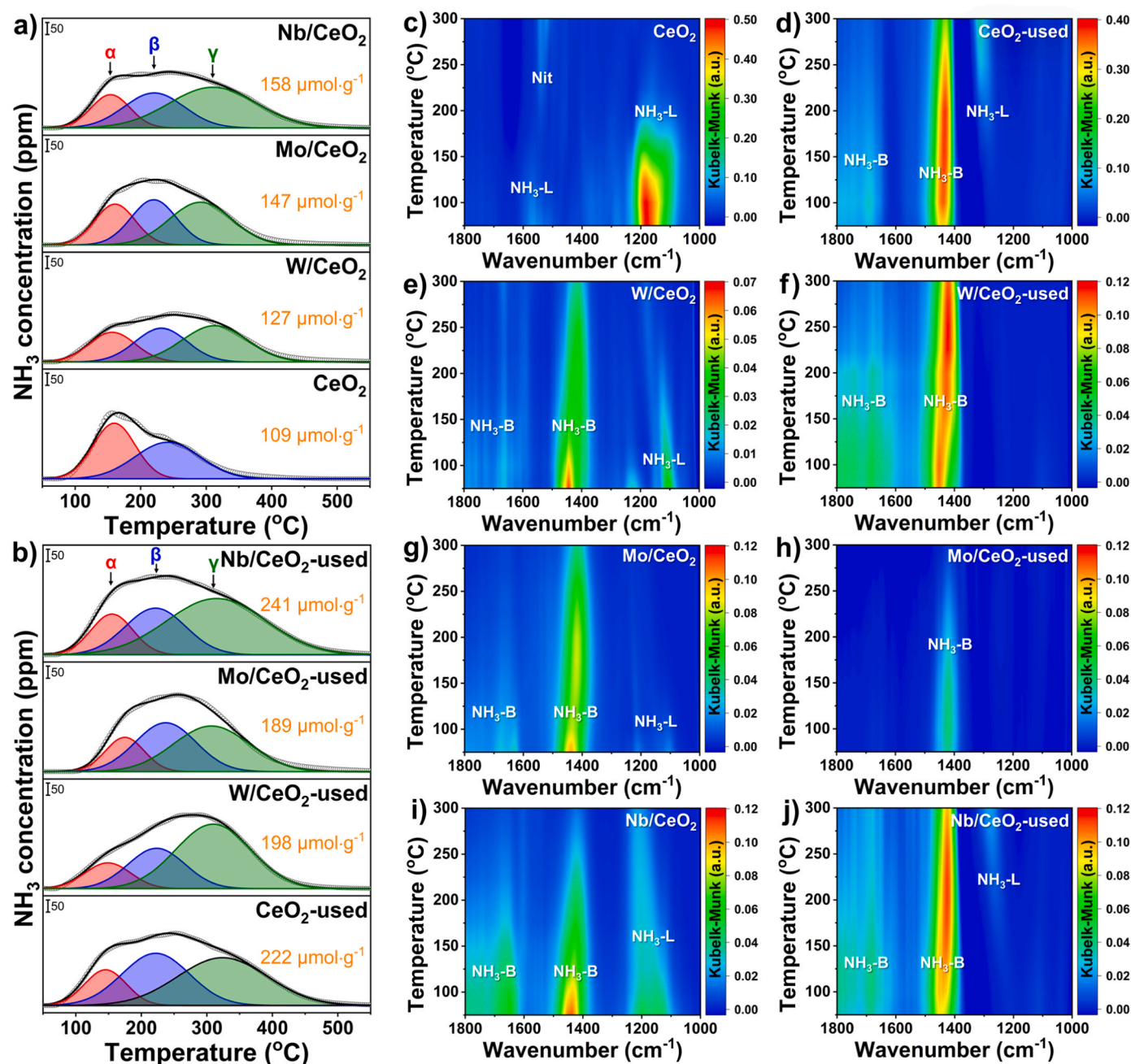


Fig. 6. NH₃-TPD profiles for a) fresh and b) used catalysts. *In situ* DRIFT of NH₃-TPD on c) CeO₂, d) CeO₂-used, e) W/CeO₂, f) W/CeO₂-used, g) Mo/CeO₂, h) Mo/CeO₂-used, i) Nb/CeO₂ and j) Nb/CeO₂-used catalysts.

OH) could trap SO_x via generating ammonium sulfate species, and thus inhibit the direct interaction between SO₂ and CeO₂. Moreover, polymeric tungsten/molybdenum oxides were stable when exposed to SO₂-containing atmosphere, and Ce coordinated with Mo showed lower reactivity with SO₂, as confirmed by the SO₂ + O₂ adsorption experiments (Fig. 1d). In contrast, for Nb/CeO₂ (Fig. 7d), fewer surface Brønsted acid sites and the reaction between polymeric niobium oxides and SO₂ would result in the deposition of more sulfate species, which accounted for the weaker SO₂ resistance of Nb/CeO₂ comparing to W/CeO₂ and Mo/CeO₂. The lower adsorption of SO₂ on Mo/CeO₂ in NH₃-SCR reaction should be attributed to the lower reactivity of Ce coordinated with Mo (Mo-O-Ce) to SO₂ and inhibitory effect of Mo-OH on the direct interaction between SO₂ and Ce by trapping SO₂ to form ABS.

3.5. Reaction mechanism

In situ DRIFTS of NO + O₂ reacting with pre-adsorbed NH₃, and NH₃ reacting with pre-adsorbed NO_x species were conducted at a relatively low temperature of 175 °C to determine the active sites and reveal the reaction mechanism. Since Mo/CeO₂ and W/CeO₂ showed similar surface adsorption properties (Fig. 6), to simplify the workload, Mo/CeO₂ and Nb/CeO₂ were selected as the research objects. As shown in Fig. 8a, after the introduction of NO + O₂ flow to Mo/CeO₂ pre-adsorbed with NH₃, the intensity of the bands assigned to NH₃-L species (1183 and 1229 cm⁻¹) decreased rapidly and these two peaks vanished in 5 min, while NH₃-B species (1420 cm⁻¹) showed relatively lower reactivity to NO + O₂, indicating that NH₃-L species were more reactive than NH₃-B [59,60]. The consumption of NH₃ could also be well demonstrated by the change of IR bands at 2500–3500 cm⁻¹, ascribed to the adsorbed

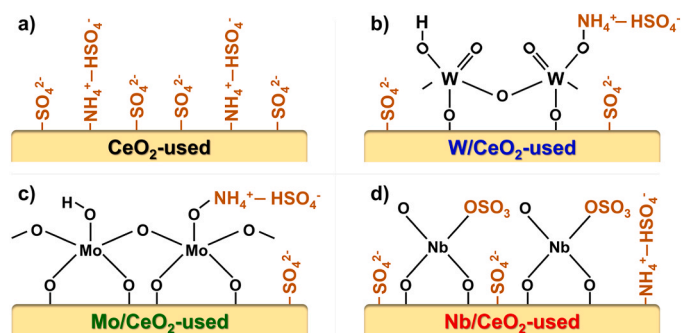


Fig. 7. Proposed surface states of a) CeO_2 -used, b) W/CeO_2 -used, c) Mo/CeO_2 -used and d) Nb/CeO_2 -used catalysts. For simplicity, all ammonium species were presented in the form of ammonium bisulfates.

NH_3 species as well [56]. It was interesting to see that almost no adsorbed NO_x species were formed on Mo/CeO_2 in 30 min, suggesting that the highly dispersed MoO_x species could effectively inhibit the adsorption of NO_x , and the NH_3 -SCR reaction on Mo/CeO_2 mainly followed Eley-Rideal (E-R) mechanism. For Nb/CeO_2 , both NH_3 -L species (1126 and 1210 cm^{-1}) and NH_3 -B species (1420 cm^{-1}) showed superior reactivity in $\text{NO} + \text{O}_2$ flow, which were all consumed in 6 min (Fig. 8b). That's why Nb/CeO_2 showed slightly higher NH_3 -SCR activity than Mo/CeO_2 at low temperature. When Nb/CeO_2 was saturated with NO_x , $\text{NO} + \text{O}_2$ flow was switched off and Nb/CeO_2 was purged by N_2 flow to remove weakly adsorbed NO_x . Afterwards, NH_3 flow was introduced to the DRIFTS cell again to investigate the reactivity of NO_x -ad species. Although the intensity of the band attributed to chelating bidentate nitrate species (1571 cm^{-1}) decreased slightly with the introduction of NH_3 , the band related to bridging bidentate nitrate species (1594 cm^{-1}) was enhanced simultaneously, indicating that the adsorbed nitrate species on Nb/CeO_2 would undergo a transformation instead of consumption when exposed to NH_3 [61–63]. So, the NH_3 -SCR reaction on both Mo/CeO_2 and Nb/CeO_2 catalysts was proceeded by E-R mechanism.

To further understand the evolution of surface states of the catalysts in the presence of SO_2 , *in situ* DRIFTS of NH_3 -SCR + SO_2 experiments

were performed (Fig. 9). For Mo/CeO_2 , NH_3 -L and NH_3 -B species were observed when exposed to NH_3 -SCR flow, and no identifiable bands related to nitrate species could be found, further suggesting that the adsorption of NO_x on Mo/CeO_2 was inhibited. Upon the introduction of SO_2 to the feeding gas, a broad band centered at 1122 cm^{-1} emerged on Mo/CeO_2 , which was attributed to sulfate species and enhanced with reaction time [29,44]. Moreover, it was found that the intensity of bands attributed to NH_3 -B species increased with the introduction of SO_2 , which could be due to the formation of sulfated species serving as Bronsted acid sites, matching well with the results of NH_3 -TPD. The enhancement in the bands related to NH_3 -B species also occurred on Nb/CeO_2 when exposed to NH_3 -SCR + SO_2 flow. Although the overlap of bands assigned to sulfates species and NH_3 -L made it difficult to directly observe the interaction between SO_2 and Lewis acid site, *in situ* DRIFTS of NH_3 -TPD results well proved that SO_2 would react with Lewis acid sites and then result in the vanishment of Lewis acid sites. Remarkably, different from what was observed on Mo/CeO_2 , multiple IR bands attributed to sulfated species (1007 , 1025 , 1091 , 1126 , 1154 , 1240 , 1270 and 1294 cm^{-1}) were observed on Nb/CeO_2 [29,44], which could be due to that SO_2 could interact with both Nb and Ce sites as discussed in Raman spectra section (Fig. 3b).

As illustrated in Fig. 10, the reactivity of adsorbed NH_3 species on sulfated catalysts (after the test shown in Fig. 9) were also evaluated. NH_3 -B species on sulfated Mo/CeO_2 were found to be still reactive to $\text{NO} + \text{O}_2$ flow, however, it would take ca. 30 min to complete the consumption of NH_3 (Fig. 10a), confirming that SO_2 would result in the deactivation of Mo/CeO_2 . As for Nb/CeO_2 , the surface sulfation also led to the decrease in the reactivity of adsorbed NH_3 species, and NH_3 -B species on sulfated Nb/CeO_2 even showed lower reactivity than those on sulfated Mo/CeO_2 , in good consistence with the results of SO_2 resistance test (Fig. 1b). It should also be noted that the change in the intensity of IR bands assigned to various sulfate species on Nb/CeO_2 could be due to the consumption of NH_3 adsorbed on sulfated species linked to Nb sites. Since no band attributed to nitrate species emerged throughout the test, it could be concluded that the NH_3 -SCR reaction on Mo/CeO_2 and W/CeO_2 followed E-R mechanism before and after sulfation treatment.

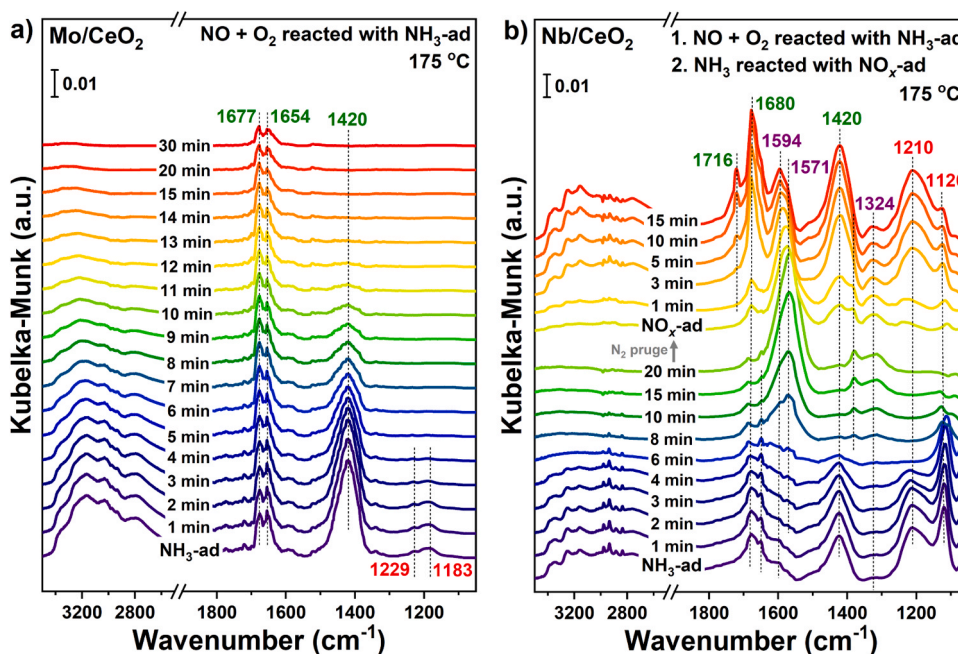


Fig. 8. a) *In situ* DRIFTS of $\text{NO} + \text{O}_2$ reacting with pre-adsorbed (NH_3 -ad) NH_3 on Mo/CeO_2 catalyst. b) *In situ* DRIFTS of $\text{NO} + \text{O}_2$ reacting with NH_3 -ad and NH_3 reacting with pre-adsorbed NO_x (NO_x -ad) on Nb/CeO_2 catalyst.

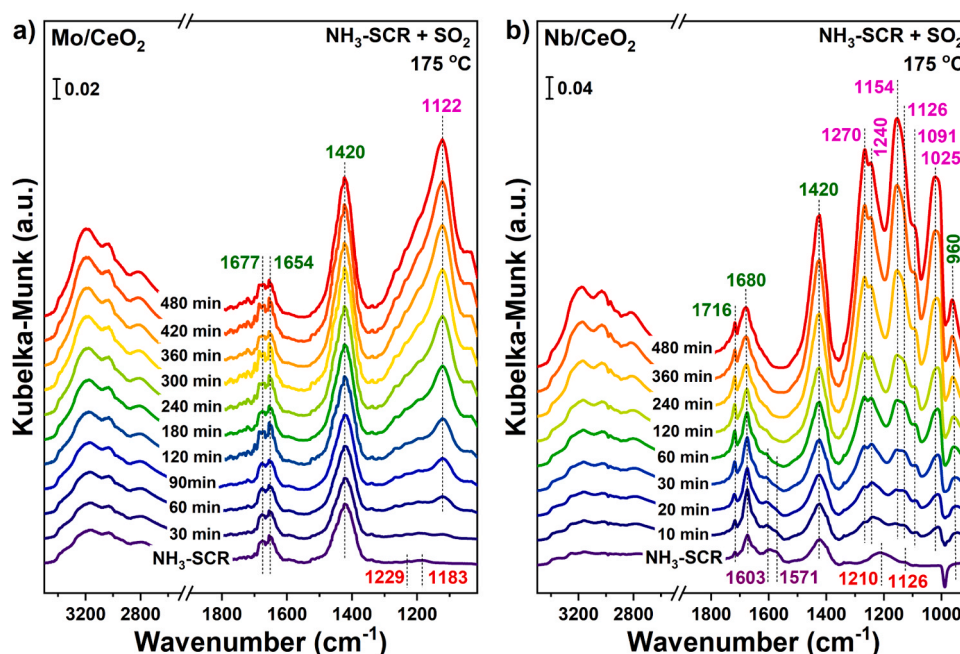


Fig. 9. *In situ* DRIFTS of $\text{NH}_3\text{-SCR} + \text{SO}_2$ on a) Mo/CeO_2 and b) Nb/CeO_2 .

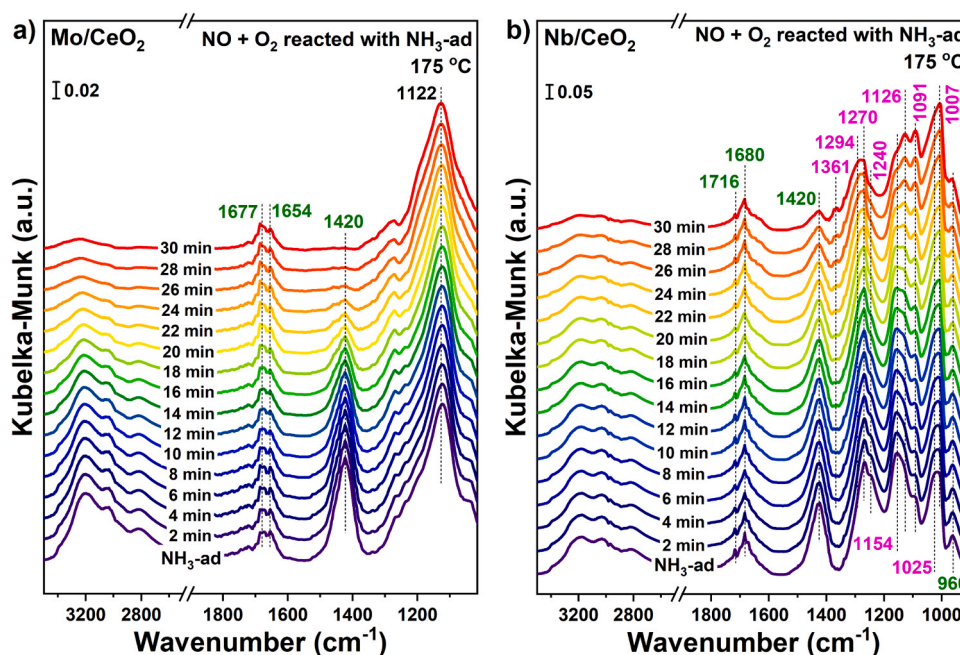


Fig. 10. *In situ* DRIFTS of $\text{NO} + \text{O}_2$ reacting with pre-adsorbed $\text{NH}_3\text{-ad}$ on a) sulfated Mo/CeO_2 and b) Nb/CeO_2 . The sulfation treatment was conducted as shown in Fig. 9.

3.6. Regeneration and the Role of Ammonium Sulfates

As discussed above, the deposition of ammonium sulfates or the sulfation of active sites would result in the deactivation of W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts. In industrial applications, calcination treatment has been widely applied for the regeneration of poisoned catalysts. Considering that ammonium sulfates deposited on W/CeO_2 , Mo/CeO_2 and Nb/CeO_2 catalysts could decompose at low temperatures ($\leq 400^\circ\text{C}$), W/CeO_2 -used, Mo/CeO_2 -used and Nb/CeO_2 -used catalysts were calcined at 400°C (lower than the calcination temperature after the impregnation of acid metal species onto CeO_2) in Ar flow for 2 h to investigate whether the removal of ammonium sulfates could help

regenerate the poisoned catalysts. As shown in Fig. 11 and Fig. S9, after the regeneration treatment (400°C , Ar flow), the NO_x conversions on W/CeO_2 -used, Mo/CeO_2 -used and Nb/CeO_2 -used catalysts at 175°C were all found to increase. Since SO_2 would not be released but re-captured by catalysts when ammonium sulfates decomposed, it could be concluded that ABS showed a much more significant poisoning effect on CeO_2 and CeO_2 modified with acid metal oxides than the sulfation of CeO_2 . The amount of sulfate species on the regenerated catalysts was further determined by TG experiments (Fig. S10). It was found that the weight loss assigned to the decomposition of sulfate species on those regenerated catalysts was almost the same as that on corresponding used catalysts, well supporting the viewpoint that SO_2 generated by the

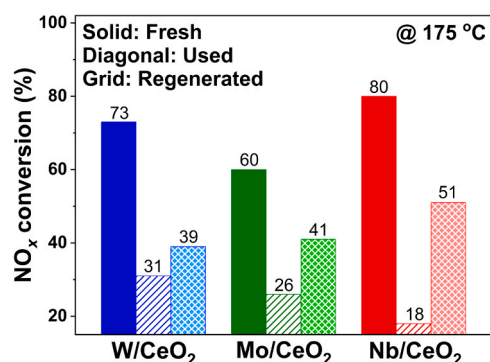


Fig. 11. NO_x conversions on fresh, used and regenerated catalysts at 175 °C.

decomposition of ammonium sulfates would be re-captured when the calcination temperature was 400 °C or lower. However, it must be noted that the calcination treatment (400 °C) might result in the deep sulfation of active sites, especially Ce species [46]. That's why the regenerated catalysts still showed poorer catalytic performance than fresh catalysts. Considering that Mo/CeO₂ showed lower reactivity to SO₂ to form sulfated CeO₂, and the deposition of ammonium sulfates was the main reason for the deactivation of Mo/CeO₂ in NH₃-SCR when exposed to SO₂, Mo-CeO₂ catalysts might show promising application perspective in some reactions in the presence of SO₂ but without NH₃.

4. Conclusion

In this work, optimal loadings of acid metal oxides (MoO₃, Nb₂O₅, WO₃) were impregnated onto CeO₂ to investigate the impact of acid metal oxide modification on CeO₂ catalyst for NH₃-SCR of NO_x. Besides the expected improvement of the activity and N₂ selectivity, significantly enhanced SO₂ resistance ability was also achieved on the CeO₂ modified with acid metal oxides comparing to bare CeO₂. Moreover, highly dispersed Mo or W species were found to better shield CeO₂ from SO₂ poisoning than highly dispersed Nb species. Besides serving as Brønsted acid sites for NH₃ adsorption/activation, highly dispersed Mo and W species could also inhibit SO₂ from directly interacting with the catalysts. It was also revealed that the consumption of highly active Lewis acid sites by SO₂ and the coverage of active sites by the deposited ammonium sulfates were the main reasons for the deactivation of CeO₂ catalysts modified with acid metal oxides. The lowest affinity of Mo/CeO₂ catalysts for SO₂ made surface Mo-O-Ce paired site an attractive element in constructing NH₃-SCR catalysts with high SO₂ resistance performance. This work provided a deep insight into designing efficient catalysts working under an SO₂-containing atmosphere.

CRediT authorship contribution statement

The manuscript was written through the contributions from all authors. All authors have given approval to the final version of the manuscript.

CRediT authorship contribution statement

Yandi Cai: Methodology, Investigation, Validation, Data curation, Writing – original draft. **Bifeng Zhang:** Methodology, Validation. **Haowei Yu:** Methodology. **Xiaoyu Ji:** Methodology. **Jingfang Sun:** Writing – review & editing. **Xizhang Wang:** Resources, Methodology. **Qihui Qian:** Investigation. **Lulu Li:** Writing – review & editing. **Annai Liu:** Methodology. **Wei Tan:** Supervision, Conceptualization, Investigation, Validation, Data curation, Writing – original draft, Writing – review & editing. **Fei Gao:** Supervision, Conceptualization, Writing – review & editing. **Lin Dong:** Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123424.

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